

Transformation Pathways and Energetics in Plutonium

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Fig. 1. Transformation pathway from fcc to monoclinic via a simple hexagonal intermediate. Atoms move continuously from fcc to the hexagonal via a common trigonal subgroup. Sixteen primitive hexagonal cells then combine to form the 16-atom monoclinic cell, a process mediated by phonons that break translational symmetry.

An outstanding problem in Pu science is understanding the mechanism of the structural transformation from the high temperature face-centered cubic (fcc) δ phase to the low temperature monoclinic α phase. The transformation is accompanied by changes in the shape of the unit cell and numbers of atoms within the unit cell. Thus, a combination of strains and displacement modes (the order parameters) are involved in describing these transformations, and the challenging problem is to obtain the atomic pathways from one crystal structure to another. This information is necessary if we are to obtain a faithful free-energy potential (and hence phase diagram) in terms of the order parameters for the transformation.

The problem is highly nontrivial as the nature of the transformation mechanism depends crucially on orientation relationships between the structures, and therefore a solution requires exploring myriad symmetry relationships among the structures. However, with the aid of large symmetry databases, and by integrating ideas from metallurgy to phonon physics, we have recently demonstrated that the transformation can be accomplished via an intermediate hexagonal structure with specific strains and displacements [1]. Figure 1 shows one of two possible paths from fcc to the monoclinic via the simple hexagonal intermediate. The trigonal three-atom unit cell is the common subgroup between the fcc and the simple hexagonal, and the arrows indicate the displacement of atoms from the fcc. At their end positions, the atoms are located at a simple hexagonal lattice and 16 primitive simple hexagonal unit cells combine to form a 16-atom unit cell that subsequently distorts to the α unit cell.

Fig. 2. The predicted mechanism is consistent with anomalies in the experimental phonon dispersion (arrows in the inset) for δ Pu. The fcc and hexagonal Brillouin zones are embedded with the appropriate orientation and the ovals are predicted locations of anomalies.

Transformation path via simple hexagonal intermediate

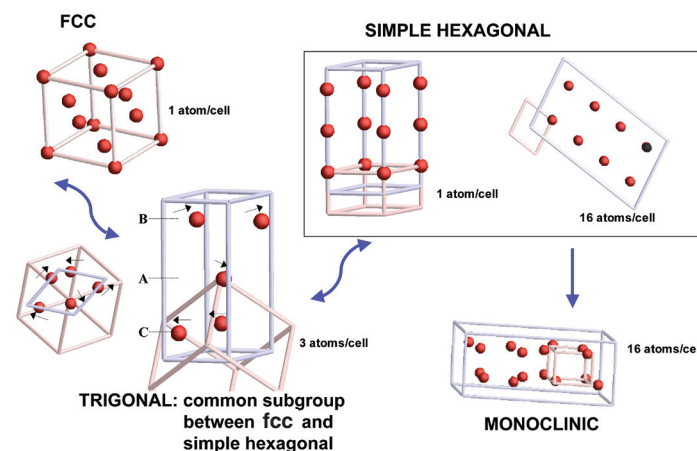
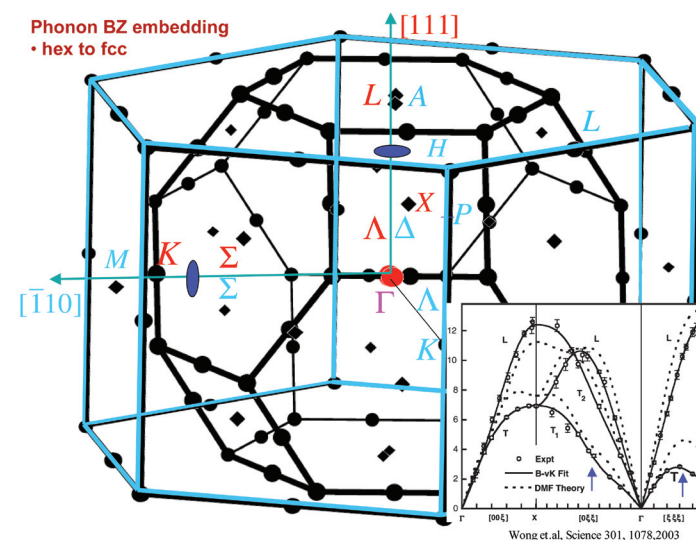


Figure 2 (inset) shows the phonon dispersion data for the δ phase (black lines) as compared to the predictions of dynamical mean field calculations (dashed lines). The anomalies in the experimental data suggesting instabilities or softening in specific directions (away from the δ and towards α) are indicated by arrows. The locations of these anomalies are consistent with the



predictions from our mechanism, and are shown by the blue ovals in the combined embedding of the fcc and hexagonal Brillouin zones that takes into account the orientations of the two crystal structures. Of the two pathways we have predicted, only energy calculations can determine which of these would be favored. Figure 3 shows the result for the volume and energy for the two candidate pathways (via simple hexagonal and hexagonally closed packed [hcp]) from a molecular statics calculation [2] using the modified embedded atom potential (MEAM). The path via the hcp is clearly energetically preferred, and the calculation shows that the volume change occurs in the second step, from the intermediate to the monoclinic. The work points to difficulties with the MEAM potential from the intermediate to the monoclinic structure and illustrates the need for reliable electronic structure calculations for Pu.

Our work implies that orientation relations in actinides severely restrict transformation pathways, so that the problem of obtaining a free energy to describe the process becomes tractable. Moreover, Pu sits at a threshold of a change in character of the orientation relationship from lighter to heavier actinides, correlating with changes in the character of electron itinerancy, magnetism, and volume.

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[1] T. Lookman, A. Saxena, R.C. Albers, *Phys. Rev. Lett.* **100**, 145504 (2008).

[2] R. Groger, T. Lookman, A. Saxena, *Phil. Mag. B* March (2008). arXiv:0812.0985 on lanl.arXiv.org

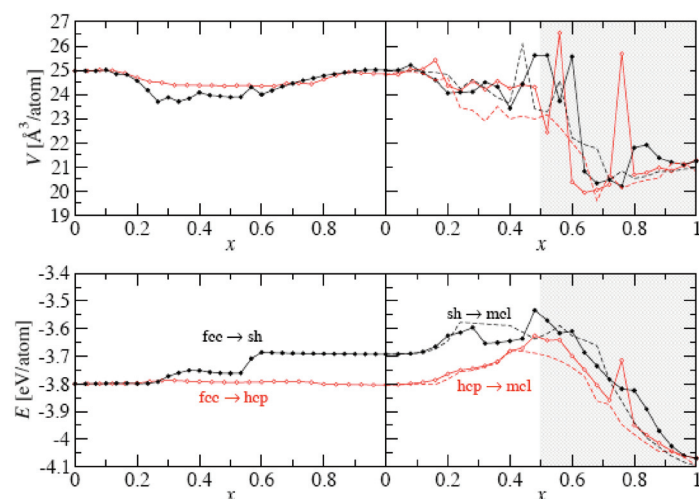


Fig. 3. Energy and volume calculated as a function of atomic displacements from fcc ($x = 0$) to the intermediate hexagonal and then to the monoclinic, using the MEAM potential for Pu. The favored intermediate structure is the hcp and the volume change occurs in the second step from the hexagonal to monoclinic symmetry.

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